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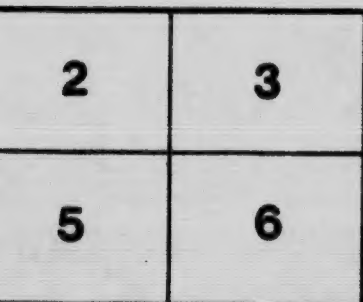
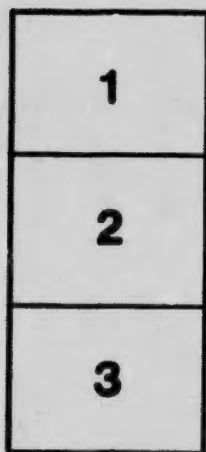
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**PAPERS FROM THE CHEMICAL
LABORATORIES**

**No. 72: THE EFFECT OF ACETONE ON THE TRANSPORT
NUMBERS OF SODIUM AND POTASSIUM CHLORIDES IN
AQUEOUS SOLUTION, BY HENRY F. LEWIS**

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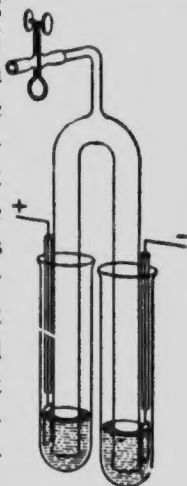
THE EFFECT OF ACETONE ON THE TRANSPORT NUMBERS OF SODIUM AND POTASSIUM CHLORIDES IN AQUEOUS SOLUTION

BY HENRY F LEWIS

The migration of a number of salts has been studied in solutions in alcohol, glycerine, methyl alcohol, etc., and in every case the transport number was found to be within a few percent of that in pure water. Salts dissolved in mixtures of alcohol and water have also been studied from this point of view with the same result.¹ The following experiments which show that the ratio u/v for the ions of potassium chloride and sodium chloride in aqueous solution is more than halved by addition of acetone are therefore of considerable interest, and must be taken into account in all attempts to interpret the electrical conductivities of these solutions.

The Apparatus

The apparatus with which I worked is not adapted to give results of a very high order of accuracy; as will be seen from the table the results of individual experiments differed by as much as 4 units in the second decimal place. The accuracy was, however, sufficient for the purpose in view, which was to make sure that the transport number is really affected by the presence of acetone; and as the apparatus is easily put together, and determinations may be made with it rapidly, I have thought it worthy of being described, and have detailed a number of test experiments made with it which show that the results of my measurements were not affected by errors due to diffusion or mixing.



¹ An index to the literature of migration determinations in solvents other than water is contained in J. W. McBain's. "Experimental data of the quantitative determinations of electrolytic migration." Trans. Wash. Ac. Sci., 9, 1 (1907).

About 200 cc of solution were used in each experiment. The U-tube was filled by suction, and the pinch-cock closed; the electrodes were then inserted, and connected with a silver voltameter and the source of current. In one experiment a Weston millammeter was used as well as the voltameter; readings were made at one minute intervals during the hour and a half that the electrolysis lasted, and the number of coulombs so obtained agreed within 0.5 percent with that given by the voltameter.

When the electrolysis was at an end, about 12 cc were withdrawn for analysis from the tube *m* ("middle portion"). The pinch-cock on *m* was then slightly opened, and the liquid in the U-tube allowed to run slowly into the electrode tubes, the U-tube being raised so that it never dipped deeply into the liquids in the electrode tubes; the cathode was removed and rinsed into the cathode tube with a little unelectrolyzed solution; these solutions were then removed, cooled, and analyzed.

Thus the anode and cathode portions were easily separated without the use of diaphragms or taps; the legs of the U-tube were rinsed out with the unaltered middle portion of the electrolyte; a middle portion was readily obtained for analysis, and gas bubbles or changes in density at the electrodes could not produce harmful stirring.

The following experiments were made to test the reliability of the apparatus; a decinormal solution of sodium chloride in 50 percent acetone was used.

1. *Diffusion of Alkali from the Cathode.*—A little litmus was added to the solution and turned pink by a trace of acid. After electrolyzing for an hour and a half the blue zone at the cathode extended less than a centimeter into the upright tube.

2. *Diffusion of Acid from the Anode.*—Methyl orange and a little alkali added to the electrolyte gave a yellow solution which after a quarter of an hour was quite red at the anode. In another hour the solution in the anode glass

was bleached, the red remained in the upright tube about 1 centimeter above the liquid in the glass.

3. *Diffusion of Chlorine.*—Indigo added to the electrolyte was bleached at the anode, but at the end of an hour and a quarter the bleaching had not extended appreciably into the upright tube.

4. *Evaporation of Acetone from the Electrode Glasses.*—A tube was set up in the usual manner, but no electricity was passed through. A Bunsen burner was set near the apparatus so that it might be as warm as during an electrolysis. After two hours the liquid was removed from one side, made up to 100 cc, and analyzed in the usual way; 93.18 cc of the silver solution were required instead of 92.74.

The Method of Analysis

Fifty cc of the unelectrolyzed solution, or 10 cc of the middle portion, were evaporated to dryness on the waterbath to remove acetone; the residue was dissolved in water, 1 cc of a neutral solution of potassium chromate added, and the chlorine determined by decinormal silver nitrate. The cathode solution after electrolysis was made up to 100 cc with unelectrolyzed solution and evaporated as before; the alkali was then neutralized with decinormal sulphuric acid, using methyl orange as indicator, and before titrating with silver a drop of decinormal alkali was added to restore the yellow color. Blank analyses showed that the method was reliable.

The chlorides and the acetone were C. P. preparations of Merck; all measuring vessels and burettes were calibrated.

Results of the Measurements

All the solutions experimented with were approximately decinormal with respect to the salt. The first column of the table gives the parts by volume of acetone in one of the solution. The second, the weight of silver (W) deposited in the voltameter. The third, the duration of the electrolysis in minutes. The fourth, the amount of decinormal silver nitrate required to precipitate the chlorine in 100 cc of the unelectro-

TABLE I

Salt	Parts of acetone	Grams of silver W	Time. Minutes	Analyses		Difference L	Change in middle	H
				Before	After			
NaCl	0	0.1875	45	90.94	79.66	10.28	—	0.59
	$\frac{1}{8}$	0.1662	60	89.08	80.66	8.42	0.00	0.55
	$\frac{1}{4}$	0.1342	60	95.20	80.48	8.60	0.05	
	$\frac{1}{2}$	0.1006	65	93.32	89.08	6.12	0.02	0.52
	$\frac{3}{4}$	0.0622	60	89.68	88.35	6.85	—0.03	
					89.69	3.63	—0.04	0.38
					89.89	3.43	0.02	
					87.43	2.25	0.04	0.38
					87.52	2.16	0.08	
KCl	0	0.1586	40	98.02	90.91	7.11	0.14	0.49
					90.64	7.38	0.09	
	0	0.1928	60	95.12	86.52	8.60	0.12	0.48
	0	0.1232	45	95.12	89.43	5.69	0.03	0.49
	0	0.2020	55	93.31	84.28	9.03	0.18	0.48
	$\frac{1}{8}$	0.1942	60	96.78	88.94	7.84	0.10	0.44
	$\frac{1}{4}$	0.1844	65	93.20	86.93	6.27	0.00	0.37
					86.69	6.51	0.03	
	$\frac{1}{2}$	0.2020	55	101.14	93.22	7.92	—0.17	0.42
	$\frac{3}{4}$	0.1154	60	99.90	95.65	4.25	0.03	0.39
					95.87	4.03	0.05	
	$\frac{1}{8}$	0.1232	45	96.22	92.22	4.00	0.02	0.35
	$\frac{1}{4}$	0.0832	75	96.70	94.01	2.69	0.02	0.32
	$\frac{1}{2}$				94.38	2.32	—0.03	
	$\frac{3}{4}$	0.0768	60	100.16	97.98	2.18	—0.04	0.29
					98.24	1.92	—0.03	

lyzed solution; and the fifth, the silver required by the 100 cc of solution obtained by adding unelectrolyzed solution to the cathode solution as explained on page 571. Column six gives the difference between the last two, that is, the loss (L) of chlorine from the cathode compartment. The seventh column gives the loss or gain in the 10 cc middle portion, expressed as cubic centimeters of the decinormal silver. The last column gives the transport number (H) of the chlorine, computed by the formula

$$H = 0.0108 L/W.$$

When 1.0 tubes were electrolyzed in series with the same solution in each, the numbers in the first four columns are the same for each, and are not repeated in the table. The fourth and twelfth electrolyses in the KCl series were carried out in series with each other; likewise the fifth and ninth.

These results show clearly that the transport numbers of the salts investigated are much lower in solutions containing acetone than in pure water, although they do not agree well enough among themselves to fix definitely the amount of the decrease.

In conclusion, I desire to express my thanks to Professor W. Lash Miller at whose suggestion these measurements were undertaken in the Spring of 1906, and to the authorities of the University of Toronto for the use of the electrochemical laboratory.

*The University of Toronto,
May, 1907.*

